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Project Title:	Energy Efficient Processes For Making Tackifier Dispersions Used To Make Pressure Sensitive Adhesives
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Recipient organization:	West Virginia University Research Corporation On behalf of West Virginia University 886 Chestnut Ridge Road P.O. Box 6845 Morgantown, WV 26506
Partners:	Mays Microsystems Inc. (Cost Share partner) Tulane University Dyna-Tech Adhesive Inc (Cost Share partner) IKA Works, Inc. (Cost share partner) Argonne National Laboratory
Technical Contact:	Rakesh Gupta (PI) (304) 293-2111 ext. 2427 Rakesh.Gupta@mail.wvu.edu
Business Contact:	Alan Martin (WVU Business Officer) (304) 293-3998 Alan.Martin@mail.wvu.edu
DOE Project Officer:	Bill Prymak (DOE Project Officer) (303) 275-4931 bill.prymak@go.doe.gov
DOE HQ Contact:	Dickson Ozokwelu (202) 586-8501 Dickson.Ozokwelu@ee.doe.gov

Executive Summary

The primary objective of this project was to develop an energy efficient, environmentally friendly and low cost process (compared to the current process) for making tackifier dispersions that are used to make pressure-sensitive adhesives. These adhesives are employed in applications such as self-adhesive postage stamps and disposable diapers and are made by combining the tackifier dispersion with a natural or synthetic rubber latex. The current process for tackifier dispersion manufacture begins by melting a (plastic) resin and adding water to it in order to form a water-in-oil emulsion. This is then converted to an oil-in-water emulsion by phase inversion in the presence of continuous stirring. The resulting emulsion is the tackifier dispersion, but it is not concentrated and the remaining excess water has to be transported and removed. The main barrier that has to be overcome in the development of commercial quality tackifier dispersions is the inability to directly emulsify resin in water due to the very low viscosity of water as compared to the viscosity of the molten resin. In the present research, a number of solutions were proposed to overcome this barrier, and these included use of different mixer types to directly form the emulsion from the molten resin but without going through a phase inversion, the idea of forming a solid resin-in-water suspension having the correct size and size distribution but without melting of the resin, and the development of techniques of making a colloidal powder of the resin that could be dispersed in water just prior to use. Progress was made on each of these approaches, and each was found to be feasible. The most appealing solution, though, is the last one, since it does not require melting of the resin. Also, the powder can be shipped in dry form and then mixed with water in any proportion depending on the needs of the process. This research was conducted at Argonne National Laboratory, and it was determined the new process uses 78% less energy than the conventional process. Additional benefits of the new process are that it can process resins that cannot presently be processed without using solvents and that it can result in new products made with mixed resins.

Accomplishments

As stated in the original research proposal, the objectives of the proposed research included the development of one or more cost effective, energy efficient and environmentally friendly processes to produce commercial quality tackifier dispersions containing resins having a range of softening points from 40^{O}C to 100^{O}C or higher. The research was organized around five different tasks having increasing levels of risk. A comparison between the actual accomplishments and each of these objectives is given below.

Task 1: Improvement of the Current Process

This task was the responsibility of West Virginia University and DynaTech Adhesives. As part of this task, an instrumented mixer was built at WVU, and a picture of the entire set up is given in Figure 1. Using this system, it was possible to measure electrical conductivity, stirrer torque, and power consumption during the course of tackifier dispersion synthesis process. All the work was done with a 25°C softening-point rosin ester system. The effect of variables such as the jacket temperature, the rate of water addition, the paste time, the amount of KOH added, the acid number of the rosin ester, and the final acid number of the recipe formulation on the point of phase inversion, and on the viscosity and mechanical stability of the tackifier dispersion was examined in detail. It was found that the indication of phase inversion by conductivity measurements agreed with visual observations. Although it was found that the viscosity of the final product could be lowered by increasing the jacket temperature, increasing the paste time, utilizing a higher final acid number or reducing the amount of KOH, the only result of commercial significance was the one related to the amount of KOH used. Indeed, lower KOH levels (or lower soap concentrations) resulted in significantly lower viscosities, and less water needed to be added to reach the point of phase inversion. This result has actually been used to formulate low viscosity, commercially useful adhesives by DynaTech.

Figure 1. Photograph of the instrumented mixer built at West Virginia University.

A significant amount of work was also done at WVU with a rotor-stator mixer with a view towards grinding an aqueous slurry of solid rosin to directly give a dispersion of the right concentration and size distribution. The rosins used were a petroleum hydrocarbon resin and a synthetic resin. Slurries of these resins (solids) in water, both with and without surfactants, were passed through the mixer several times. When surfactants were not used, there was significant agglomeration of the particles. Even in the presence of a surfactant, the mean particle size could not be reduced below about 100 micrometers for either resin if a tackifier dispersion of the correct solids concentration was desired. The size could, however, be reduced by an order of magnitude if the solids concentration was drastically reduced, but now the dispersion was very dilute. The concentration could be boosted back up when a colloid mill was utilized, and an average particle size of the order of 10 micrometer was obtained with a 100 8C softening point resin. Also, the best results were observed when the material was recirculated under high shear, but then heat built up and the resin particles became sticky; this caused agglomeration and plugging of the mixer. It is our feeling that the use of a proper cooling system would have solved the heat transfer problem and would also have allowed us to go to lower particle sizes. This method is particularly useful for higher softening point resins that are currently found in solvent-based PSAs, because these resins soften above the boiling point of water but are easily dissolved in solvents. Note that Ross Mixing and IKA Works were involved in this portion of the research.

Task 2: Direct emulsification of resin in water using an Extensional Flow Mixer (EFM).

This task was the responsibility of the Mays Microsystems Company, and the intention was to emulsify the molten resin in water without going through a phase inversion step. Success was achieved in using the extensional flow mixer to produce an acceptable Tackifier dispersion. The set up used is shown in Figure 2.

Figure 2. Photograph of the extensional flow mixer used with resins that are liquid at room temperature.

The rosin used was liquid at room temperature (10°C softening point). The emulsion contained 60% solids, and it was very stable. The mean particle size was marginally higher at 2.29 microns versus 1.81 micron using conventional mixing. Nonetheless it had a lower viscosity as compared to the product made by the conventional process. This means that the solid loading can be increased further without allowing the viscosity to become excessive. This tackifier dispersion was used to formulate a pressure sensitive adhesive (Formulation A) by mixing with a 2-Ethylhexyl Acrylate emulsion along with additives such as defoamers, surfactants and thickeners. It was then subjected to peel, tack and static shear tests. The results are given below, and they compare very well with corresponding results for an adhesive formulated with a conventional tackifier dispersion (Formulation B).

Property	**Formulation A**	**Formulation B**
90 Peel, Stainless steel, 30 min dwell	26 psi	28 psi
TLMI Loop tack	35 psi	41 psi
Shear Adhesion, 1”x1”	1100 min	1100 min

Strip, 1kg weight

Had funding continued to be available, this work would have been continued with higher softening point resins.

Task 3: *Comminution of resin followed by emulsification*

As part of this task in the program, Argonne National Laboratory tested two processes to grind the resin down to an average particle size of 3-5 micrometers. The resulting powder can be used to form dispersions in water in few minutes with minimal agitation and without heating the water. The processes also eliminate the need for using excess water, and allow using high temperature melting resins without using solvents. The first process involves pumping a resin/water slurry to a high pressure and then shattering the resin particles as the pressure is suddenly dropped, and the second process involves grinding the resins dry before or after cooling them using liquid nitrogen or dry ice. Experiments were conducted using three commonly used resins, one of which was a high temperature melting resin. The two processes were found to be technically feasible and economically promising. However, results proved that the grinding process is technically superior to the high pressure shattering method. In particular, the grinding process produced smaller average particle sizes and is easier to scale up. It also uses commercially available equipment. Preliminary economic evaluation of the two processes indicated that the grinding method is more economical to implement. Therefore, after the initial work, attention was focused on the grinding method. At the end of two years, the best results were obtained with a resin having a softening point of 100 8C, and these are shown in Figure 3. In the 500 pound test, the average particle size was 2.47 micrometers and the maximum particle size was under 10 micrometers.

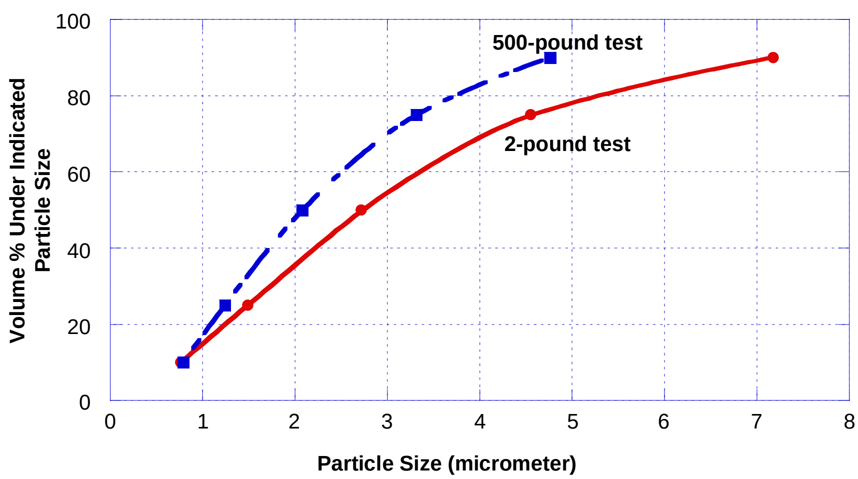

Figure 3. Results of tests conducted using commercial equipment.

The final results showed that it was possible to reduce the particle size of the tackifier polymers to about 2.5 micrometers which meets the criteria for success. Cooling the chips using liquid N_2 would reduce the particle size further, if this were needed.

Task 4: *Single-Step Synthesis of PSAs*

This work was done at DynaTech adhesives by students from WVU. The intention was to make the intermediate step of tackifier dispersion synthesis redundant by developing a single-step process of making the pressure-sensitive adhesive. This avoids the necessity of making the tackifier dispersion in a first step and then adding it to a rubber latex in a second step. The approach that was taken was to substitute water that would normally be added to the tackifier dispersion by the rubber latex that provides the adhesive action. Although we were able to synthesize a tackifier dispersion with a 62 wt% solid content (as opposed to the normal 56 wt%) with acceptable tack, peel and shear strength properties in the final adhesive, work on this task was stopped mid-way through the program because it was felt that this approach was not likely to be commercialized in view of the success attained with the use of the other approaches.

Task 5: *Rheological Characterization*

Standard tackifier dispersion samples as well as those developed as part of this program were sent to Tulane University for rheological characterization. Measurements of shear viscosity, normal stresses, dynamic mechanical properties and hysteresis were made at room temperature. An AR 2000 cone and plate viscometer made by the TA Instruments company was used. While some samples were stable under all conditions of measurement, other samples were unstable and coagulated with increasing deformation rate. In the range of conditions at which measurements could be made, the different samples were highly shear-thinning, and the rheology was dominated by viscous rather than elastic properties. Viscosity data could be represented by the four parameter Cross equation, so that the viscosity η is expressed as:

$$\eta = \eta_0 \frac{1+\theta \dot{\gamma}^m}{1+\beta \dot{\gamma}^m}$$

where η_0 is the zero shear viscosity, θ, β and m are model parameters. Note that no meaningful primary normal stress difference data could be obtained, indicating that the samples were not elastic.

Summary of Project Activities

A four-pronged approach was taken to achieve the project objectives – (i) The current process was examined to understand the kinetics and thermodynamics of the system. Results have allowed the DynaTech Company to change their process and optimize it, but the total energy savings have not been large. (ii) A totally new mixer type, an extensional flow mixer, was employed, with success, to synthesize the tackifier dispersion without going through a phase inversion step. (iii) Another approach was to pass a concentrated slurry of plastic pellets through an appropriate mixer to obtain a dispersion having particle sizes in the tens of micron range. (iv)

The final approach was to use a dispersion of resin in water without going through the melting and phase inversion steps by comminution followed by emulsification.

Thus, all the original hypotheses were validated, and the result has been the identification of three potential processes for making tackifier dispersions. The extensional flow mixer at Mays efficiently produced dispersions of low softening point resins directly in water. The average droplet size obtained was about 2 microns, and the adhesive that was formulated with this dispersion was satisfactory. This technique was to be extended to higher softening point resins with the use of an extruder to melt the resin. Unfortunately, work had to be stopped since funding was curtailed, and Mays did not receive any money beyond the first year of the project. It should be emphasized that we see no technical barriers to completely achieving the objectives outlined in the proposal.

High shear equipment at IKA Works, was shown to give rapid reduction of resin particle sizes directly in water. However, the reduction in particle size was accompanied by a rapid rise in temperature with attendant particle agglomeration. Had the project funding been maintained at original levels, a heat exchanger would have been built to remove heat and run the mixing equipment in a continuous manner. The major success of this approach was that it gave a dispersion of the correct solids concentration using both low softening and high softening point resins.

The Argonne National Laboratory process was technically the farthest along the road to success when funding was eliminated. It produced powders having an average size of the order of a micrometer, and these could be dispersed in water to give practically useful pressure-sensitive adhesives. Had the project maintained its momentum, this process would have been the obvious choice for commercialization.

Presentations made

1. R.K. Gupta and others, Energy efficient processes for making tackifier dispersions used to make pressure-sensitive adhesives, AIChE Spring National Meeting, New Orleans, LA, April 25-29, 2004.
2. R.K. Gupta and others, Processes for making tackifier dispersions used in the synthesis of pressure-sensitive adhesives, AIChE Spring National Meeting, Atlanta, GA, April 11-12, 2005.
3. D. Song and R.K. Gupta, Experimental study of the process for making tackifier dispersions used in pressure-sensitive adhesives, AIChE Annual Meeting, San Francisco, CA, November 12-17, 2006.